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M. Zawadzki, T.M. Runge, and A.J. Ragauskas

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Investigation of *Ortho*- and *Para*-Quinone Chromophores in Alkaline Extraction Stage Residual Lignins

Michael Zawadzki, Troy Runge, and Arthur Ragauskas
Institute of Paper Science and Technology, 500 10th St., NW, Atlanta, Georgia, 30318

The chromophoric properties of a series of residual lignins were studied in order to understand brightness development during pulp bleaching. This study focused upon lignins isolated from kraft softwood brownstock, chlorine dioxide delignified brownstock, and a series of oxidative alkaline extracted pulps. The chromophoric properties of the isolated lignins were assessed by both visible absorbance and ^{31}P-NMR spectroscopy. A ^{31}P-NMR spectroscopic method was employed for the quantification of the combined *ortho*- and *para*-quinone content in the isolated lignins. The ^{31}P-NMR method, modified from the literature, utilized the derivatization of lignin quinone structures by trimethylphosphite. The results suggest that chromophores, such as *ortho*- and *para*-quinones, may be important contributors to brightness ceiling development during chemical pulp bleaching.

A number of structures have been implicated as chromophores in mechanical and chemical pulps, including: catechol-metal complexes [1-4], coniferaldehyde [1,2,5], quinone methides [1], stable radicals [1] and quinones [1,2,4,6-9]. Of the various possible chromophores, quinones have been suggested to be major contributors to the color of kraft lignin [6-8,10]. This study employed visible absorbance spectroscopy and a ^{31}P-NMR-based procedure to investigate the presence of quinone chromophores in residual lignin isolated from bleached kraft pulps. The generation of quinone structures during chlorine dioxide bleaching and their fate during oxidative alkaline extraction were explored.

Chemical Pulp Bleaching. Multistage bleaching consists of delignification and brightening stages. In the delignification bleaching stage, bulk residual lignin is degraded and removed. Chlorine dioxide (D), as a delignification agent, is replacing chlorine (C) or chlorine/chlorine dioxide (C/D) because of environmental pressures to reduce adsorbable organic halide (AOX) formation.

Contemporary bleaching sequences use alkaline extraction (E) after a chlorine dioxide (D) stage to remove oxidized lignin and increase the efficiency of a subsequent chlorine dioxide stage. The primary function of the alkaline extraction stage is thought to involve solubilization of oxidized lignin fragments by conversion of various functional

groups to their ionized forms: carboxylate, phenolate, and enolate anions [11]. Oxidants, such as hydrogen peroxide (P) and oxygen (O), are often applied in the alkaline extraction stage to further assist with delignification and increase pulp brightness.

The final brightening stages are responsible for the elimination of residual chromophoric structures. The chromophoric structures may be initially present both in the pulp and/or formed during the preceding bleaching sequences. During the final brightening stages of bleaching, the residual lignin concentration is low. Therefore, during brightening, the elimination of the chromophoric structures must be highly selective or else cellulose damage will take place.

Quinone Chemistry. Lignin quinone structures are important because of their chromophoric properties and because they may be concurrently formed and destroyed during bleaching. For example, chlorine dioxide has been shown by several investigators [12-18] to react with phenolic lignin structures giving *ortho-* and *para*-quinone structures among its products. Conversely, hydroperoxide anion, generated during hydrogen peroxide bleaching, specifically removes conjugated carbonyl structures such as quinones [19-21]. Quinones may also be formed by the Dakin reaction of hydrogen peroxide with *para*-hydroxy carbonyl structures [19,22].

During alkaline oxygen bleaching, hydroxyl radicals may generate lignin-hydroxycyclohexadienyl radicals which lead to quinone formation *via* disproportionation or demethoxylation [23]. Alternatively, given the presence of superoxide anion, the hydroxycyclohexadienyl radical may be degraded to muconic acid structures.

Lignin model compound studies have also shown *ortho*-quinones to be susceptible to nucleophilic attack by hydroxide anions. *Ortho*-quinone structures may rearrange to an α-hydroxy-carboxylic acid cyclopentadiene structure by a benzylic acid type of rearrangement [19]. Also, hydroxide may add to quinone structures by nucleophilic addition to give precursors of chromophoric hydroxy-substituted quinones [19,24].

Materials and Methods

Chemicals. All chemicals, except 1,4-dioxane, were purchased and used as received. Before use, 1,4-dioxane was purified by distillation over sodium borohydride.

Pulps. Conventional kraft pulp was obtained from a single, 30-year-old, disease-free Loblolly pine (*Pinus taeda*) tree. Brownstock pulp (kappa number 30.5) was bleached in a D_0 stage under the following conditions: 2.3% chlorine dioxide charge, 10% consistency, 45°C, final pH=2.0, and 45 minute reaction. The bleached pulp was then washed with water and characterized for kappa number, Klason lignin content, and viscosity.

Alkaline Extraction. Chlorine dioxide (D_0) delignified pulp was alkaline extracted in a stirred pressure reactor under the following general conditions: 10% consistency, 70°C, and 75 minute reaction. **Table I** summarizes the specific conditions used for the oxidative alkaline extraction study. Washed alkaline extracted pulps were characterized in terms of kappa number, Klason lignin content, and pulp viscosity.

Table I. Alkaline Extraction Stage Conditions.

Stage	Bleaching Conditions[a]
E	2.0% NaOH charge; atmospheric pressure air.
E+O	2.5% NaOH charge; 60 psig oxygen initially, decreased by 12 psig/5 minutes.
E+P	2.5% NaOH charge; 0.5% hydrogen peroxide charge.
E+O+P	2.5% NaOH charge; 0.5% hydrogen peroxide charge; 60 psig oxygen initially, decreased by 12 psig/5 minutes.
E+Ar	Oxygen was removed from the pulp slurry by a freeze-thaw cycle; 2.0% NaOH charge; slight applied pressure (~10 psig) with argon.

[a] final pH > 10.5

Brightness Ceiling Determination. The alkaline extracted pulps were further bleached with a D_1ED_2 sequence. The D_1 stage conditions were as follows: 0.75% chlorine dioxide charge, 10% consistency, 70°C, and 3-hour reaction. E_2 stage conditions were as follows: 1.0% sodium hydroxide charge, 10% consistency, 70°C, and 60-minute reaction. Washed E_2 stage pulps were bleached in a D_2 stage. Chlorine dioxide charge in the D_2 stage was varied from 0.2% to 0.8% charge in a series of separate experiments. A small amount of sodium hydroxide (25% of chlorine dioxide charge added) was added at the D_2 stage for pH adjustment.

Isolation of Residual Lignin. Residual lignin was isolated from the pulps by a mild acidic dioxane hydrolysis procedure modified from the literature [25-28]. Pulp was extracted using 90% 1,4-dioxane/0.1 N HCl (v/v) solution (8% consistency) by refluxing for 2 hours under an argon atmosphere. The extract was filtered, neutralized, and 1,4-dioxane was removed under reduced pressure at 40°C. The resulting aqueous lignin solution was acidified (pH 2.5) to precipitate the lignin. The precipitated lignin was purified by three cycles of a freeze-thaw-centrifuge-decant sequence. The purification sequence involved freezing the aqueous lignin sample (-20°C), slow thawing, centrifugation, decanting, and washing the lignin with water. Between each cycle the pH of the solution was adjusted to 2.5. The yield of residual lignin, relative to Klason lignin, was 45-65%. Purified lignin was freeze-dried and analyzed by visible absorbance spectroscopy and ^{31}P-NMR spectroscopy after trimethyl phosphite derivatization.

Visible Spectrum of Lignin. The visible absorbance spectra of isolated lignins were measured in 90% 1,4-dioxane/water (v/v) solvent. The visible absorbance spectra were acquired with a Shimazdu UV160U ultraviolet/visible spectrophotometer.

Pulp Characterization. The lignin contents were measured by both a ¼ kappa number test (TAPPI T 236 om-85) and a modified standard Klason lignin content test (TAPPI T 222 om-88). The Klason lignin content test used an autoclave to speed up the sulfuric acid digestion of the pulp. Viscosity of cupriethylenediamine (CED) dissolved pulp was measured by TAPPI method T 230 om-94. Standard TAPPI handsheets were prepared from D_2 stage pulp (basis weight of 150 g/m^2) and used to measure ISO brightness (TAPPI T 205 sp-95).

Quinone Determination. Dry residual lignin (30 mg) was derivatized with 500 μL 50% trimethyl phosphite/DMSO (v/v) under an argon atmosphere at room temperature for seven days. Lignin samples were previously dried under vacuum (3 millitorr) at 40°C for 24 hours.

Derivatized lignin samples were prepared for analysis by removing excess trimethyl phosphite under vacuum at 40°C for 3 hours. The treated lignins were dissolved in 400 μL of solvent consisting of DMSO-d_6, tri-*m*-tolyl-phosphate (2.5 mg/mL) and chromium acetylacetonate (1.0 mg/mL). Derivatized lignin quinone structures were hydrolyzed to the open-chain phosphate ester by the addition of 5 μL water (0.3 mmol per 30 mg lignin). After 12 hours, the ^{31}P-NMR spectrum of the resulting solution was acquired with a Bruker 400 MHz NMR spectrometer.

Phosphorus-NMR spectra were acquired under quantitative conditions at 305°K. A 90° pulse was utilized with a 5-second pulse delay along with inverse-gated broad-band proton decoupling. A line-broadening factor of 15 Hz was used and the time domain (TD) size was 64K. For each spectrum 1000-3000 scans were collected. The internal standard tri-*m*-tolyl-phosphate (-16.3 ppm) was used both for quantification and as a shift reference. The ^{31}P-NMR chemical shift of tri-*m*-tolyl-phosphate in DMSO-d_6 was determined with the aid of 85% H_3PO_4 as an external shift reference. Quantification of lignin quinone content was achieved by integrating the areas of the internal standard and the phosphate-ester (quinone adduct) resonance centered at -2.5 ppm.

Chromium acetylacetonate was used to reduce the T_1 (spin-lattice) relaxation of the components of interest including the internal standard. The T_1 value for the open-chain phosphate ester (quinone adduct) in trimethyl phosphite treated lignin was found to be 0.7 seconds. The T_1 relaxation time constant for the internal standard, tri-*m*-tolyl-phosphate, was found to be 0.9 seconds. A standard inversion-recovery experiment [29] was used to determine the T_1 parameters.

Results and Discussion

Pulp Characterization. Lignin contents of the bleached pulps were determined by both Klason lignin and kappa number tests and are shown in **Table II**. In general, a higher degree of delignification occurs with increased application of oxidant in the alkaline extraction stage. The CED viscosity data, which is an indirect measure of cellulose

degradation, is also given in **Table II**. The viscosity data reveals that only minor carbohydrate damage occurs during the bleaching stages. In the alkaline extraction stage, hydrogen peroxide was more selective towards lignin removal than oxygen on the basis of Δkappa per Δviscosity (using brownstock for the initial values).

Table II. Pulp Characterization Data.

Pulp Description	Kappa Number	Kalson Lignin	CED viscosity
Brownstock	30.4	1.895	30.27
D	14.6	1.583	26.40
D(E+Ar)	7.10	0.768	25.72
DE	6.37	0.709	22.57
D(E+O)	4.17	0.661	20.10
D(E+P)	4.80	0.671	22.64
D(E+O+P)	3.33	0.589	20.38

Brightness Ceiling. A brightness ceiling is the maximum brightness that can be achieved in a given bleaching stage after which further application of bleaching agent does not lead to an increase in brightness. The various alkaline extracted pulps were further bleached with a D_1ED_2 sequence to generate a D_2 brightness ceiling (**Figure 1**).

The D_2 brightness ceiling data reveals that the use of hydrogen peroxide in the alkaline extraction stage, D(E+P) and D(E+O+P), results in the highest achievable brightness ceilings. When excluding all oxygen with argon, D(E+Ar), or incorporating air, D(E), or reinforcing with pressurized oxygen, D(E+O), in the alkaline extraction stage gives similar D_2 brightness ceiling values. **Figure 1** demonstrates that pulp properties altered in the first alkaline extraction stage directly impact the bleachability of the pulp. Specifically, hydrogen peroxide decreases the content of structures which have a detrimental influence on the final brightness ceiling value.

Previous chemical pulp bleaching studies have investigated parameters influencing brightness ceiling values. For example, McDonough found that brightness ceiling development during D_2 stage bleaching (of a $D_0(E+O)D_1ED_2$ sequence) is dependent upon D_1 stage brightness [30]. In further studies of the $D_0(E+O)D_1ED_2$ bleaching sequence, McDonough *et al.* found that at a constant kappa factor the D_2 brightness ceiling is affected by the unbleached kappa number and the effective alkali charge during pulping [31]. These results suggest that lignin structural features may influence final brightness ceiling values.

Senior *et al.* showed that the brightness ceiling of a DEDP sequence is greater than that of a DEPD sequence [32]. Senior *et al.* hypothesized that the higher brightness ceiling of the DEDP sequence is due to the presence of quinone or conjugated-carbonyl chromophores which survive the DED sequence only to be removed when hydrogen

peroxide stage is subsequently applied [32]. Similarly, the results of this investigation suggest that hydrogen peroxide, applied in the alkaline extraction stage, removes quinone (or conjugated carbonyl) structures that would otherwise cause a lower D_2 brightness ceiling value.

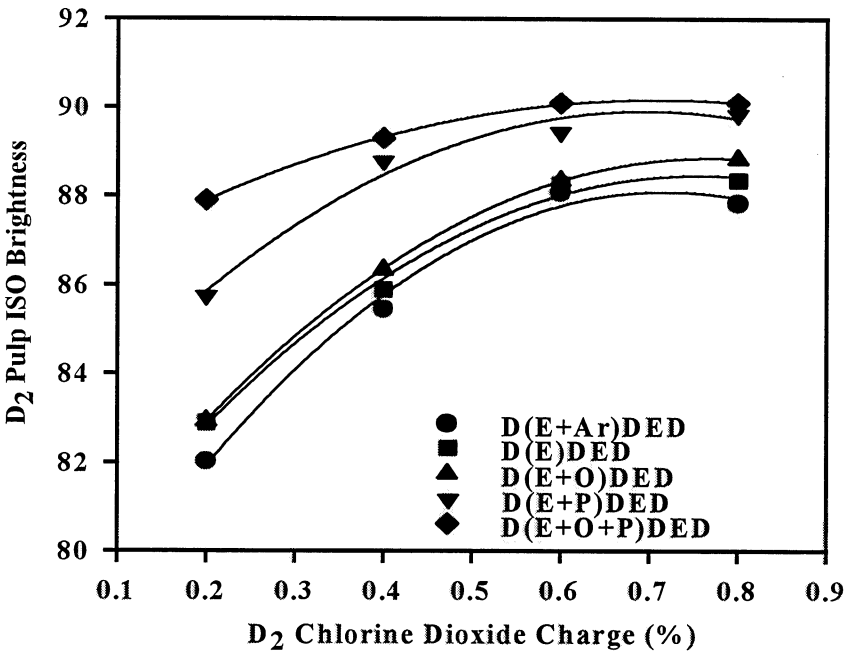


Figure 1. D_2 Stage Brightness Ceiling Data.

Visible Spectrum. The visible absorbance difference spectra for the series of residual lignins isolated from chlorine dioxide delignified brownstock and oxidative alkaline extracted pulps were acquired (**Figure 2**). Difference spectra were calculated by subtracting the brownstock residual lignin absorption spectrum from the absorption spectra of the isolated lignins. Analysis of difference spectra allows for the identification of chromophore changes occurring in the alkaline extraction stage relative to the unbleached brownstock.

Clearly, the absorbance difference spectra are observed to cluster into groups based upon the oxidant applied to the alkaline extraction stage. Residual lignins arising from peroxide-treated pulps displayed considerably less visible absorbance than the initial unbleached brownstock residual lignin. Note that with the exception of hydrogen peroxide bleaching, D(E+P) and D(E+O+P), all residual lignins are darker than the initial brownstock residual lignin (**Figure 2**).

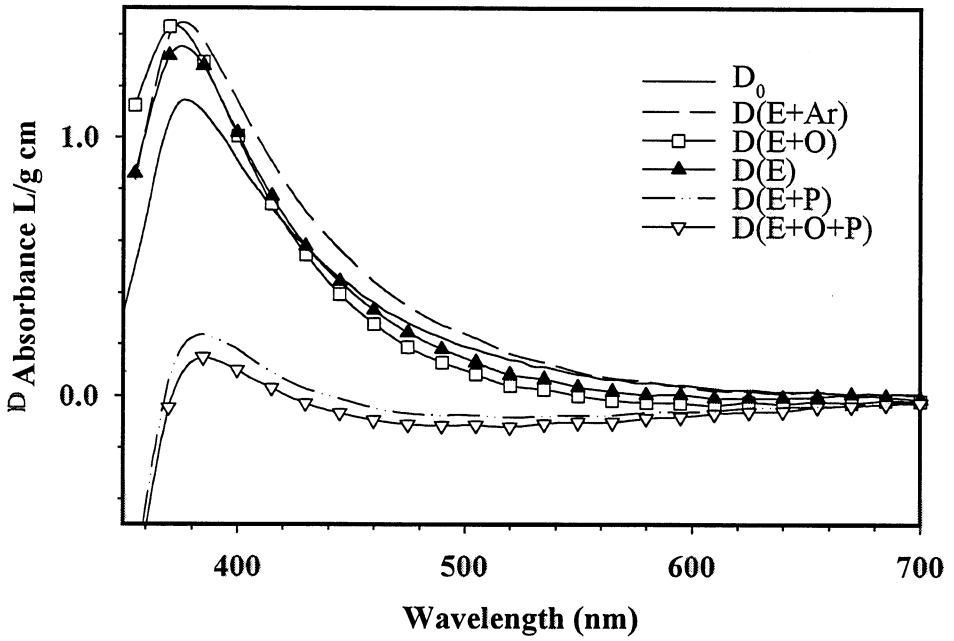


Figure 2. Visible Absorption Difference Spectra for a Series of Residual Lignins.

Quinone structures are potential chromophoric contributors to the brightness ceiling phenomena. The $n-\pi^*$ transition for quinones occurs in the visible region and may contribute to the colored nature of pulps. In general, the $n-\pi^*$ transition for *para*-quinones occurs in the 420-460 nm region and 500-580 nm for *ortho*-quinones [33]. According to Furman and Lonsky, the absorption maximum for kraft lignin quinone structures occurs at ~430 nm [8]. If the residual lignins are ordered in terms of absorbance at 430 nm the following series is derived: D(E+Ar) > D = D(E) > D(E+O) >> D(E+P) > D(E+O+P). It can be noted that this order corresponds to the brightness ceiling results shown in **Figure 1**. The correlation between brightness ceiling values and absorption spectra at the alkaline extraction stage indicates that lignin structural features of a chromophoric nature may be carried through from a previous bleaching stage and directly impact the final brightness value. These results suggest that lignin quinone structures may be important chromophoric contributors to the brightness ceiling values.

Trimethyl Phosphite Chemistry

***Ortho*-Quinone Derivatization.** Both *ortho*- and *para*-quinones are known to form adducts with trimethyl-phosphite [34-36]. The reaction of trimethyl phosphite with the *ortho*-quinone 3,5-di-*tert*-butyl-1,2-benzoquinone (I) is shown in **Figure 3**. Attack of the trimethyl phosphite phosphorus at the carbonyl is thought to initially give a zwitterionic structure (II). Cyclization of II then leads to a benzo-dioxaphospholene structure (III) [34,36-38]. The phosphorus chemical shift value, determined in this study (-45.3 ppm, DMSO-d_6 solvent), for the benzo-dioxaphospholene is similar to previously reported values: -46.5 ppm (CD_2Cl_2 solvent) [37] and -46.9 ppm ($CDCl_3$ solvent) [36].

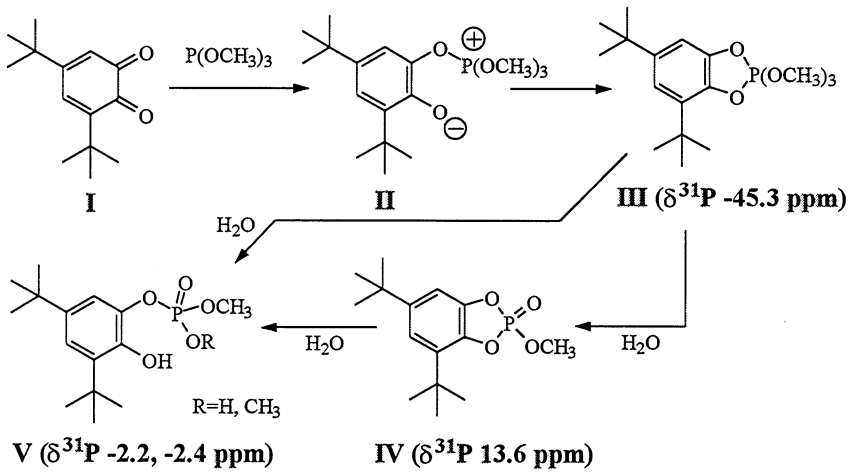
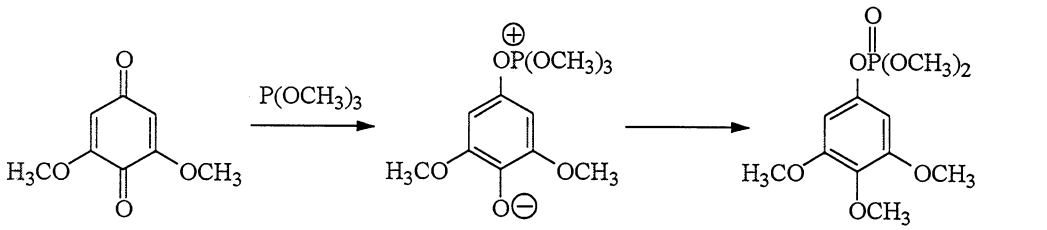


Figure 3. Reaction of Trimethyl Phosphite with 3,5-Di-*tert*-butyl-1,2-benzoquinone (^{31}P Chemical Shifts were Determined in this Study; DMSO-d_6 Solvent).

The benzo-dioxaphospholene adduct can be hydrolyzed to give a cyclic phosphate ester (IV, **Figure 3**) [34,38]. The phosphorus chemical shift value determined for cyclic phosphate ester was found to be 13.6 ppm (DMSO-d_6 solvent) and this value is similar to that reported by Medvecz (13.4 ppm, CD_2Cl_2 solvent) [37]. During the present investigation it was found that the cyclic phosphate ester (IV) is unstable and further hydrolysis leads to a structure with a chemical shift similar to the open-chain phosphate ester. The expected structure of the cyclic phosphate ester hydrolysis product is V (R=H) [39].

An open-chain phosphate ester adduct (V, **Figure 3**) can also result from the direct action of water on the benzo-dioxaphospholene adduct [37]. Two possible isomeric open-chain phosphate esters products (V, R=CH_3) may be formed. The phosphorus chemical shift values (-2.2 and -2.4 ppm, DMSO-d_6 solvent) for the open-chain phosphate esters were found to be similar to a reported value of -4.0 ppm ($CDCl_3$ solvent) [36]. Medvecz reported a similar phosphorus chemical shift for the open-chain phosphate ester adduct of 3-methoxy-1,2-benzoquinone (-2.3 ppm, CD_2Cl_2 solvent) [37].

***Para*-Quinone Derivatization.** Ramierez *et al.* demonstrated that trimethyl phosphite can form an adduct with *para*-quinones [34,35]. **Figure 4** illustrates the reaction of trimethyl phosphite with the *para*-quinone 2,6-dimethoxy-1,4-benzoquinone (VI). The mechanism is thought to proceed by attack of trimethyl phosphite on the carbonyl oxygen leading initially to a phosphonium-phenoxide zwitterion (VII). Rapid methyl group translocation gives the open-chain phosphate ester in high yield (VIII) [34,35]. Two isomeric adducts may be formed depending upon which quinone carbonyl group is initially attacked. The phosphorus chemical shift value for VIII was found to be -1.4 ppm (DMSO-d_6 solvent). In a related study, Medvecz reported the phosphorus chemical shift values for the trimethyl phosphite/2-methoxy-1,4-benzoquinone isomeric adducts as -2.6 and -3.15 ppm (CD_2Cl_2 solvent) [37].



VI **VII** **VIII (δ^{31}P -1.4 ppm)**

Figure 4. Reaction of Trimethyl Phosphite with 2,6-Dimethoxy-1,4-benzoquinone (^{31}P Chemical Shifts were Determined in this Study; DMSO-d_6 Solvent).

Lignin Derivatization. Using trimethyl phosphite derivatization, Lebo and others have developed a solid-state ^{31}P-NMR spectroscopic method for the detection *ortho*-quinones [40-44]. Lebo *et al.* [40-42] and Argyropoulos *et al.* [43,44] both used the cyclic phosphate ester adduct (III, **Figure 3**) as diagnostic for the presence of *ortho*-quinones in trimethyl phosphite derivatized mechanical pulp. For this study, the literature procedure [40-44] was modified and applied to the determination of quinone structures in isolated lignins. The modification consisted of hydrolyzing the cyclic phosphate ester, *ortho*-quinone adduct (III), to the open-chain phosphate ester adduct (V). Therefore, after the addition of water, the combined lignin *ortho*- and *para*-quinone content can be determined by monitoring the open-chain phosphate ester structures with phosphorus chemical shifts in the -2.5 ppm region.

A solution ^{31}P-NMR spectrum of trimethyl phosphite derivatized D(E+Ar) residual lignin is shown in **Figure 5**. The internal standard, tri-*m*-tolyl-phosphate is observed as a sharp resonance with a chemical shift of -16.3 ppm. The broad Gaussian resonance corresponding to open-chain phosphate esters, arising from derivatized quinone structures, are observed with a peak centered at -2.5 ppm. Resonances downfield from the open-chain phosphate ester correspond to trimethyl-phosphate (3.5 ppm, verified with pure material) and an expected series of phosphate esters arising from trimethyl phosphite hydrolysis [45,46].

Lignin Quinone Content. The combined *ortho*- and *para*-quinone content data (after subtraction of the softwood brownstock residual lignin quinone content) for the D_0 and alkaline extraction stage residual lignins is given in **Figure 6**. The brownstock residual lignin quinone content value, 1.6 quinones per 100 C_9, determined in this study was similar to literature values for softwood kraft lignin: 3 quinones per 100 C_9 (*via* reductive acetylation) [8] and 3-4 quinones per 100 C_9 (*via* visible absorbance) [47]. The ^{31}P-NMR derived quinone content data (**Figure 6**) was found to cluster into groups in a manner similar to the visible difference absorbance data (**Figure 2**). The lowest quinone contents were observed when the alkaline extraction stage was reinforced with hydrogen peroxide, D(E+P) and D(E+O+P) (**Figure 6**), and this corresponds to the highest achievable brightness ceilings (**Figure 1**).

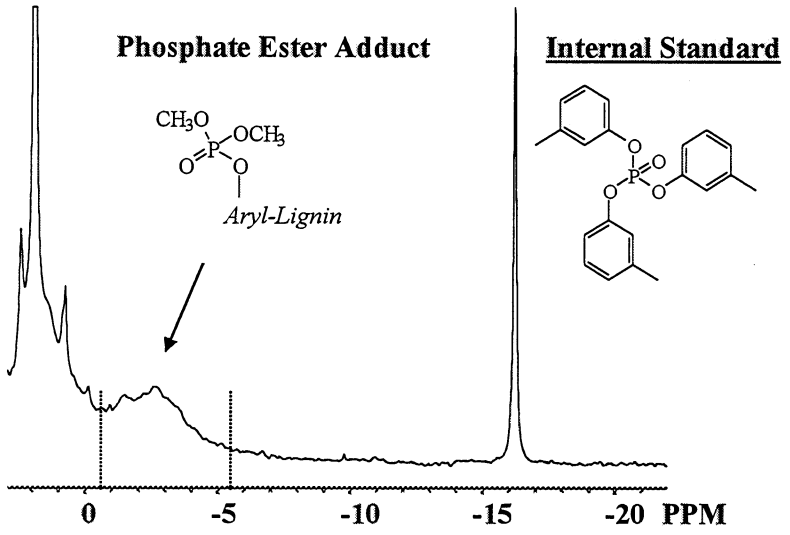


Figure 5. Phosphorus-NMR Spectrum of D(E+Ar) Residual Lignin Treated by Trimethyl-Phosphite.

Chlorine Dioxide Stage. The application of chlorine dioxide (D_0) was found to cause a dramatic increase in the quinone content relative to the brownstock residual lignin value (**Figure 6**). The D_0 residual lignin contained 0.135 mmol/g lignin (2.5 quinones per 100 C_9) more quinone structures than the brownstock residual lignin. These results are consistent with literature accounts which indicate that both phenolic and non-phenolic lignin structures can react with chlorine dioxide to give *ortho*- and *para*-quinones [12-18]. The ^{31}P-NMR derived quinone content data is also consistent with the visible absorption difference spectra which demonstrates that D_0 residual lignin is darker than brownstock residual lignin. Chlorine dioxide is an effective delignification agent (**Table II**), but the residual lignin is darker than the unbleached brownstock residual lignin.

Alkali Effect in the Alkaline Extraction Stage. The influence of alkali on quinone chromophores was studied by performing the alkaline extraction under an argon atmosphere, D(E+Ar). Application of alkali resulted in the destruction of 55% of the quinone content introduced at the D_0 stage (**Figure 6**). Clearly, the influence of alkali is not merely lignin solubilization, but also involves the destruction of quinone chromophores.

The visible absorbance difference spectra (**Figure 2**) reveal that the D(E+Ar) residual lignin is the darkest (λ = 430 nm) of all the studied lignins. According to the ^{31}P-NMR analysis (**Figure 6**), the D_0 stage residual lignin contains the highest quinone content and would be expected to have the greatest visible region absorbance (λ = 430 nm). One possible explanation for the apparent discrepancy between the ^{31}P-NMR and visible absorbance data may be that a portion of the quinone structures in the D(E+Ar) residual lignin are hydroxy substituted. Mechanical pulp [48] and model compound [24] studies have both suggested that hydroxy-quinone structures may contribute to the "alkali-

darkening" phenomena. The action of alkali on quinone precursors may give rise to poly-phenolic structures which may be subsequently oxidized to hydroxy-quinones.

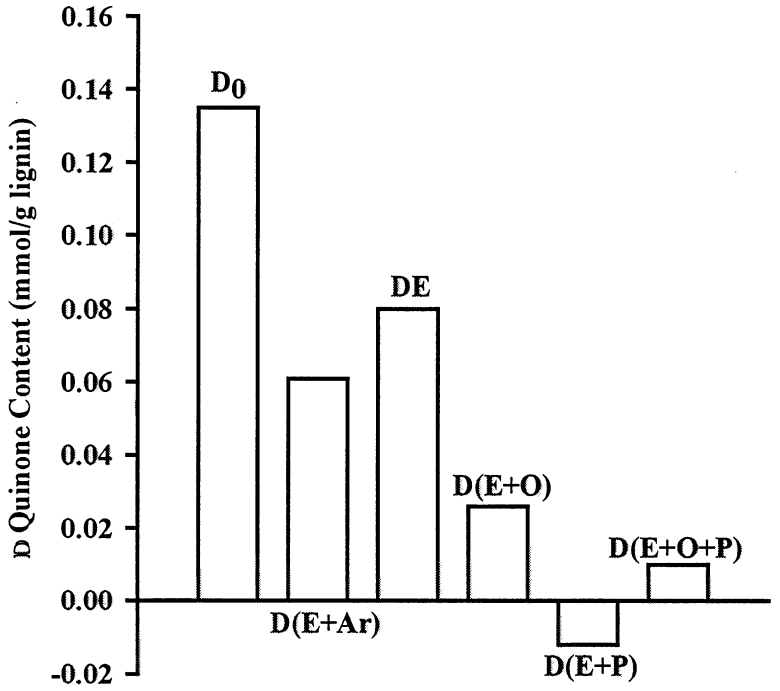


Figure 6. Residual Lignin Quinone Content Data After Subtraction of Brownstock Residual Lignin Quinone Content Value.

Table III gives spectral data, acquired in this study, for a number *para*-quinone models with various degrees of hydroxylation. The hydroxyl auxochrome causes a bathochromic shift and intensifies the π-π^* transition in the quinone chromophore [33]. Furthermore, visible absorbance spectra were acquired in aqueous dioxane solution and ionization effects also intensify the molar absorptivity of hydroxy-substituted quinones [24,33]. **Table III** shows that increased hydroxyl substitution results in greater visible region (λ = 430 nm) molar absorptivity. In particular, the spectrum of tetrahydroxy-1,4-benzoquinone was found to be characterized by a broad intense absorption throughout much of the visible region. Therefore, the data in **Table III** combined with both visible absorbance difference spectra (**Figure 2**) and ^{31}P-NMR analysis (**Figure 6**) suggests that although alkali is effective at removing lignin-quinone structures, a portion of the remaining quinones may be hydroxy-substituted and display enhanced chromophoric properties.

Table III. Visible Region Spectral Parameters for Selected Quinones.

Quinone	log $\varepsilon_{500\ nm}$ [a]	log $\varepsilon_{430\ nm}$ [a]
1,4-Benzoquinone	0.56	1.35
2,5-Dihydroxy-1,4-benzoquinone	1.35	2.33
Tetrahydroxy-1,4-benzoquinone	2.14	2.04

[a] 90% 1,4-dioxane/10% water (v/v) solvent

Oxygen Effect in the Alkaline Extraction Stage. Interestingly, incorporating air in the alkaline extraction stage, D(E), results in a greater quinone content than if only alkali is applied, D(E+Ar) (**Figure 6**). The higher quinone content of D(E) relative to D(E+Ar) can tentatively be assigned to the contribution of quinone formation during alkaline oxygen bleaching [23]. **Table II** reveals that a major benefit of incorporating air in the alkaline extraction stage is greater delignification relative to the effect of alkali alone.

When alkaline extraction is reinforced with pressurized oxygen, D(E+O), 81% of the quinone content introduced at the D_0 stage is removed (**Figure 6**). The D(E+O) residual lignin contains 0.026 mmol/g lignin (0.48 quinones per 100 C_9) more quinone structures than the brownstock residual lignin. The application of pressurized oxygen, D(E+O), *versus* air, D(E), suggests that the mechanism of quinone removal by oxygen is dependant of the oxygen concentration (pressure). The general mechanism of oxygen bleaching is known to be influenced by the concentration of oxygen [23,49].

Peroxide Effect in the Alkaline Extraction Stage. The dramatic influence of hydrogen peroxide on quinone destruction is observed in **Figure 6**. Application of hydrogen peroxide in the alkaline extraction stage, D(E+P), results in the removal of more quinone structures than were introduced at the D_0 stage. The result in **Figure 6** is consistent with the known reactivity of hydroperoxide anion towards conjugated carbonyl structures [19-21]. Although application of both hydrogen peroxide and pressurized oxygen in the alkaline extraction stage, D(E+O+P), gives a higher quinone content than hydrogen peroxide alone, D(E+P), greater delignification is a benefit of the concurrent application of both hydrogen peroxide and pressurized oxygen (**Table II**).

Conclusions

The presence of chromophores such as *ortho*- and *para*-quinones may be important contributors to brightness ceiling development during chemical pulp bleaching. This investigation further suggests that brightness ceiling values may be dependant upon the chromophore content established in earlier bleaching stages. Although quinones are only one of a number of potential chromophoric structures in kraft lignin, analyzing residual lignin quinone contents may be of valuable in understanding the origin of bleachability differences between chemical pulps.

The utility of trimethyl phosphite derivatization for investigating quinone chromophores in isolated kraft lignins was demonstrated for the first time. The results of this investigation are consistent with many of the suspected reactions of quinone structures in lignin. For example, the ability of chlorine dioxide to introduce lignin quinone structures and hydrogen peroxide to remove them was clearly observed. Further work is in progress applying ^{31}P-NMR spectroscopy towards understanding the introduction and removal of quinone chromophores in multistage bleaching sequences.

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